

NICKEL METAL HYDRIDE STORAGE BATTERY

FIELD OF THE INVENTION

[0001]

5 The present invention relates to a nickel metal hydride storage battery comprising a positive electrode including nickel hydroxide as an active material, a negative electrode including a hydrogen absorbing alloy containing aluminum, a separator and an alkaline electrolyte. More particularly, the present invention
10 relates to a nickel metal hydride storage battery of this type which is characterized in that aluminum, which is released from the hydrogen absorbing alloy containing aluminum by charge and discharge of the battery, is prevented from being deposited on the positive electrode.

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BACKGROUND OF THE INVENTION

[0002]

An alkaline storage battery has recently been used for cellular phones, electric vehicles, and the like. As the alkaline
20 storage battery, a nickel metal hydride storage battery is preferably used from the standpoints of higher capacity and improved environmental safety as compared to a nickel cadmium

storage battery.

[0003]

There is, however, a problem with a nickel metal hydride
5 storage battery that when the battery is repeatedly charged and
discharged, metal included in the hydrogen absorbing alloy which is
used for the negative electrode is partially dissolved in the
alkaline electrolyte as metal ions. These metal ions deposit on
the separator to reduce the insulation effect of the separator or
10 deposit on the positive electrode to cause self discharge, to
reduce discharge capacity of the battery, and to cause
deterioration of high rate discharge characteristics.

[0004].

15 As disclosed in Japanese Patent Laid-open Publication No. 7-
335245, an alkaline storage battery has been proposed in which a
complex-forming agent, which forms a complex with metal ions from
the hydrogen absorbing alloy dissolved in the alkaline electrolyte,
and an amine are included in the alkaline electrolyte.

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[0005]

However, even if the complex-forming agent is included in the

alkaline electrolyte, it is difficult to capture the metal ions to form a complex. Thus, there is still a problem that the metal ions deposit on the separator to reduce the insulation effect of the separator, or deposit on the positive electrode to cause self discharge, reduce discharge capacity of the battery, and cause deterioration of high rate discharge characteristics. Especially, when a hydrogen absorbing alloy containing aluminum is used, dissolved aluminum ions deposit on the positive electrode to cause self discharge, reduce discharge capacity of the battery, and cause deterioration of high rate discharge characteristics.

[0006]

It is also a problem that the complex-forming agent forms ionic impurities when it is included in the alkaline electrolyte and causes self discharge by movement of the ions between the positive and negative electrodes.

OBJECTS OF THE INVENTION

[0007]

An object of the present invention is to solve the above-described problems of a nickel metal hydride storage battery comprising a positive electrode containing nickel hydroxide as an

active material, a negative electrode containing a hydrogen absorbing alloy which contains aluminum, a separator and an alkaline electrolyte. Especially, it is an object of the present invention to improve the efficiency of capture of aluminum ions dissolved in the alkaline electrolyte in a nickel metal hydride storage battery comprising a hydrogen absorbing alloy containing aluminum, and prevent or minimize depositing of aluminum ions on the positive electrode to inhibit self discharge, reduction of discharge capacity and deterioration of high rate discharge characteristics.

SUMMARY OF THE INVENTION

[0008]

In the present invention, in order to solve the above-described problems, a complex-forming agent which forms a complex with aluminum is included in the negative electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009]

Fig. 1 is a cross section of a nickel metal hydride storage battery prepared in the Example.

[Explanation of elements]

- 1: positive electrode
- 2: negative electrode (hydrogen absorbing alloy electrode)
- 3: separator
- 4: negative electrode can
- 5: positive electrode lead
- 6: sealing lid
- 7: negative electrode lead
- 8: insulation packing
- 9: positive electrode external terminal
- 10: coil spring

DETAILED EXPLANATION OF THE INVENTION

[0010]

When aluminum included in the hydrogen absorbing alloy of a
negative electrode of a nickel metal hydride storage battery is
released from the alloy as aluminum ions during charge and
discharge of the battery, if a complex-forming agent which forms a
complex with aluminum is included in the negative electrode, the
aluminum ions are efficiently captured by the complex-forming agent
before the aluminum ions dissolve in the alkaline electrolyte and
form a complex. Movement of aluminum ions to the positive
electrode is also inhibited and deposition of aluminum ions on the

positive electrode is sufficiently prevented so as to suppress self discharge, reduction of discharge capacity and deterioration of high rate discharge characteristics. It is preferable to provide the complex-forming agent on a surface of the negative electrode to capture aluminum ions before they dissolve in the alkaline electrolyte.

5 [0011]

When the complex-forming agent is included in the negative electrode, the problem of the complex-forming agent forming ionic impurities in the alkaline electrolyte, which cause self discharge by movement between the positive and negative electrodes, is avoided.

15 [0012]

As the complex-forming agent, for example, an aromatic carboxylic acid, an amino polycarboxylic acid, and the like can be used. As the aromatic carboxylic acid chromotropic acid, sulfosalicylic acid, and the like can be used. As the amino polycarboxylic acid, trans-cyclohexane-1,2-diaminetetraacetic acid (CDTA), and the like can be used.

[0013]

The above-described complex-forming agent is easily oxidized by oxygen to create carbonate ions, nitrate ions, and the like, and it may be possible that the carbonate ions, nitrate ions, and the
5 like will likely deteriorate storage characteristics and high rate discharge characteristics. To prevent such problem, it is preferable that a layer comprising a hydroxide or oxide of an element selected from the group consisting of calcium, strontium, scandium, yttrium, lanthanoid and bismuth is formed on a surface of
10 the positive electrode active material to inhibit generation of oxygen at the positive electrode during charge of the battery. A layer comprising a hydroxide or oxide of yttrium is desirable to sufficiently inhibit generation of oxygen.

15 [0014]

Nitrate ions generated by oxidation of the complex-forming agent dissolve in the alkaline electrolyte and move between the positive and negative electrodes and cause self discharge. Therefore, a sulfonated separator which is capable of catching
20 these ionic impurities is preferably used.

DESCRIPTION OF PREFERRED EMBODIMENT

[0015]

[Example]

An example of a nickel metal hydride storage battery of the
5 present invention is described below. It is of course understood
that the present invention can be modified within the scope and
spirit of the appended claims.

[0016]

10 A cylindrical nickel metal hydride storage battery as shown in
Fig. 1 was prepared.

[0017]

As a hydrogen absorbing alloy for the active material of the
15 negative electrode, particles of $MmNi_{3.2}Co_{1.0}Al_{0.2}Mn_{0.6}$ comprising Misch
Metal (Mm), which is a mixture of rare earth elements (La, Ce, Pr
and Nd contained in a ratio by weight of 25:50:6:19), and Ni, Co,
Al and Mn, and having an average diameter of about 50 μm were used
in this Example.

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[0018]

To prepare the negative electrode a small amount of water was

added to a mixture of 100 parts by weight of the hydrogen absorbing alloy particles and 1.0 part by weight of poly(ethylene oxide) as a binder to prepare a paste. The paste was coated on both sides of a nickel plated punched metal as a current collector. The coated punched metal was dried to prepare a negative electrode in which the hydrogen absorbing alloy particles are adhered on both sides of the punched metal.

[0019]

To prepare a positive electrode a sintered nickel substrate having a porosity of 85 % was immersed in a nickel nitrate solution containing cobalt nitrate and zinc nitrate by a chemical immersing method to impregnate the sintered nickel substrate with a positive electrode active material comprising nickel hydroxide containing cobalt and zinc. Then the sintered nickel substrate was dipped in a 3 weight % yttrium nitrate solution, and was dipped in a 25 weight % sodium hydroxide solution to prepare the positive electrode in which a layer of yttrium hydroxide was formed on the positive electrode active material.

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[0020]

A polyolefin nonwoven fabric was used as a separator. 30

weight % potassium hydroxide was used as an alkaline electrolyte.

[0021]

The separator 3 was inserted between the positive electrode 1
5 and the negative electrode 2 and was rolled spirally, and was
placed in a negative electrode can 4 as shown in Fig. 1. The
alkaline electrolyte was poured into the negative electrode can 4
and the can was sealed. The positive electrode 1 was connected to
a sealing lid 6 through a positive electrode lead 5, and the
10 negative electrode 2 was connected to the negative electrode can 4
through a negative electrode lead 7. The negative electrode can 4
and sealing lid 6 were electrically insulated by an insulation
packing 8. A coil spring 10 was placed between the positive
sealing lid and a positive electrode external terminal 9. The coil
15 spring 10 is compressed and releases gas from inside of the battery
to the atmosphere when pressure in the battery unusually increases.

[0022]

20 Then the nickel metal hydride storage battery prepared in
Example 1 was charged at 100 mA for 16 hours at a temperature of 25
°C, and was discharged at 1000 mA to 1.0 V at a temperature of 25

^oC (this charge and discharge cycle is considered one cycle).

Charge and discharge of the battery were repeated for five cycles to activate the battery.

5 [0023]

The activated nickel metal hydride storage battery was charged at 1000 mA for 24 minutes, charged at 10 A for two minutes, and then was discharged at 10 A for two minutes. Charge and discharge cycles were repeated (charge and discharge at 10 A is considered one cycle). The battery was discharged to a battery voltage of 1.0 V every 1000 cycles, and was charged at 1000 mA for 24 minutes. 20,000 cycles of charge and discharge at 10 A were repeated.

[0024]

15 The positive electrodes and separators were removed from an activated nickel metal hydride storage battery not subjected to the repeated charge and discharge cycles ("the activated only battery") and from the battery subjected to the repeated 20,000 charge and discharge cycles ("the repeated cycle battery") to measure the 20 content of aluminum Al (weight %) relative to the total amount of the positive electrode and relative to the total amount of the separator. The results are shown in Table 1.

[0025]

The activated only battery and the repeated cycle battery were charged at 1000 mA for 1.2 hours and were discharged at 1000 mA to 5 1.0 V to obtain discharge capacities (mAh). The results are shown in Table 1.

[0026]

The activated only battery and the repeated cycle battery were 10 charged at 500 mA for 1.6 hours at a temperature of 25 °C and were discharged at 500 mA to 1.0 V to obtain discharge capacities Q_0 (mAh) before storage. After they were charged at 500 mA for 1.6 hours at a temperature of 25 °C, they were left at a temperature of 45 °C for 7 days and were discharged at 500 mA to 1.0 V to obtain 15 discharge capacities Q_a (mAh) after storage. A capacity maintenance rate (%) was calculated as follows:

[0027]

$$\text{Capacity maintenance rate (\%)} = (Q_a/Q_0) \times 100$$

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[0028]

The activated only battery and the repeated cycle battery were

charged at 1000 mA for 0.5 hour and were discharged at a high current of 20 A to obtain a voltage (V) of each battery after 10 seconds from starting discharge. These results are shown in Table 1 as high rate discharge characteristics.

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[0029]

Table 1

	Al Content (weight %)		Discharge Capacity (mAh)	Capacity Main- tenance Rate (%)	High Rate Discharge Character istics (V)	
	Positive Electrode	Separator				
10	Activated only battery	0.09	0.09	1000	80	1.015
15	Repeated cycle battery	0.29	0.06	800	45	0.900

[0030]

The repeated cycle battery has a higher aluminum content in the positive electrode as compared with the activated only battery.

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[0031]

In the repeated cycle battery, discharge capacity and capacity maintenance rate which is affected by discharge capacity and self

discharge, are lower than that of the battery without repeated cycles. The voltage of the repeated cycle battery when the battery was discharged at the high current is also lower than that of the activated only battery.

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[0032]

Therefore, if a complex forming agent which is capable of forming a complex with aluminum is included in a negative electrode comprising a hydrogen absorbing alloy containing aluminum, aluminum released from the hydrogen absorbing alloy is captured by formation of a complex with the complex forming agent to prevent aluminum from being dissolved in an alkaline electrolyte. Thus, deposition of aluminum ion on a positive electrode is prevented and an increased aluminum content in the positive electrode is avoided. High rate discharge characteristics, capacity, and capacity maintenance rate, which is affected by discharge capacity and self discharge, are improved.

20 [0033]

The present invention can provide significant improvements in storage characteristics, discharge capacity and high rate discharge

characteristics of a nickel metal hydride storage battery by including a complex-forming agent capable of forming a complex with aluminum in a negative electrode which includes a hydrogen absorbing alloy containing aluminum.

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[0034]

The present invention can also avoid ionic impurities generated from a complex-forming agent from being included in an alkaline electrolyte, which is a problem when the complex-forming 10 agent is dissolved in the alkaline electrolyte.